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1. INTRODUCTION

As part of the 1999 NARSTO Northeast Oxidant and Particulate Study (NE-OPS) field campaign, the DOE G-1 aircraft sampled trace gasses and aerosols in and around the Philadelphia metropolitan area. Twenty research flights were conducted between July 25 and August 11. The overall goals of these flights were to obtain a mechanistic understanding of O_3 production; to characterize the spatial and temporal behavior of photo-oxidants and aerosols; and to study the evolution of aerosol size distributions, including the process of new particle formation. Within the NE-OPS program, other groups provided additional trace gas, aerosol, and meteorological observations using aircraft, balloon, remote sensing, and surface based instruments (Phillbrick et al., 2000).

In this article we provide an overview of the G-1 observations related to O_3 production, focussing on the vertical distribution of pollutants. Ozone production rates are calculated using a box model that is constrained by observed trace gas concentrations. Highest O_3 concentrations were observed on July 31, which we present as a case study. On that day, O_3 concentrations above the 1-hour 120 ppb standard were observed downwind of Philadelphia and also in the plume of a single industrial facility located on the Delaware River south of the city.

2. EXPERIMENT AND CALCULATIONS

Philadelphia is a city of 1.4 million people in a metropolitan area of 6 million. It is part of the northeast corridor which contains the major metropolitan areas of Washington, DC, Baltimore, Philadelphia, New York City, and Boston. Winds from the SW are in approximate alignment with these cities so that a plume from the southern part of the corridor can affect areas to the north. There is a large collection of power plants in the upper Ohio River Valley to the west of Philadelphia which also can affect the city.

Flights were conducted in the mid-morning and mid-afternoon to characterize the build up of O_3 precursors early in the day and the resulting O_3 plume produced by the days photochemistry. Typical flight patterns are illustrated in Fig.1. There were 8 morning and 8 afternoon urban flights of the type shown in Fig. 1. On 6 days both morning and afternoon flights were conducted. Flight patterns were designed around an assumed southwesterly wind flow, a common direction during O_3 episodes. Under this flow condition the region in Figure 1 enclosed by a rectangle, denoted as "Urban Box", is located 20 km downwind from the center of downtown Philadelphia.

Measurements made from the G-1 included, O_3, NO, NO_y, speciated VOCs, CO, H_2O_2, organic peroxides, HCHO, aerosol parameters, actinic flux, and meteorological variables. Instrumentation is similar to that deployed on previous field campaigns. See Weinstein-Lloyd et al. (1996) for a description of peroxides, Lee et al. (1996) for HCHO, Kleinman et al. (1996) for VOCs and Nunnermacker et al. (1998) for the remaining trace gasses. Hydrocarbon samples were collected in canisters and analyzed by J. Rudolph's research group at York University for C2-C12 compounds.

Observations of O_3, CO, VOCs, NO, HCHO, H_2O_2, and organic peroxides have been used as inputs to a constrained steady state (CSS) box model calculation. The CSS model is described by Kleinman et al. (1997) and uses a chemical mechanism from Stockwell et al. (1990) and Paulson and Seinfeld (1992). Calculations yield the concentrations of rapidly reacting species (OH, HO_2, speciated RO_2's, and NO_2) which are in equilibrium with measured species. We also obtain rates, including the production rate of O_3, $P(O_3)$.

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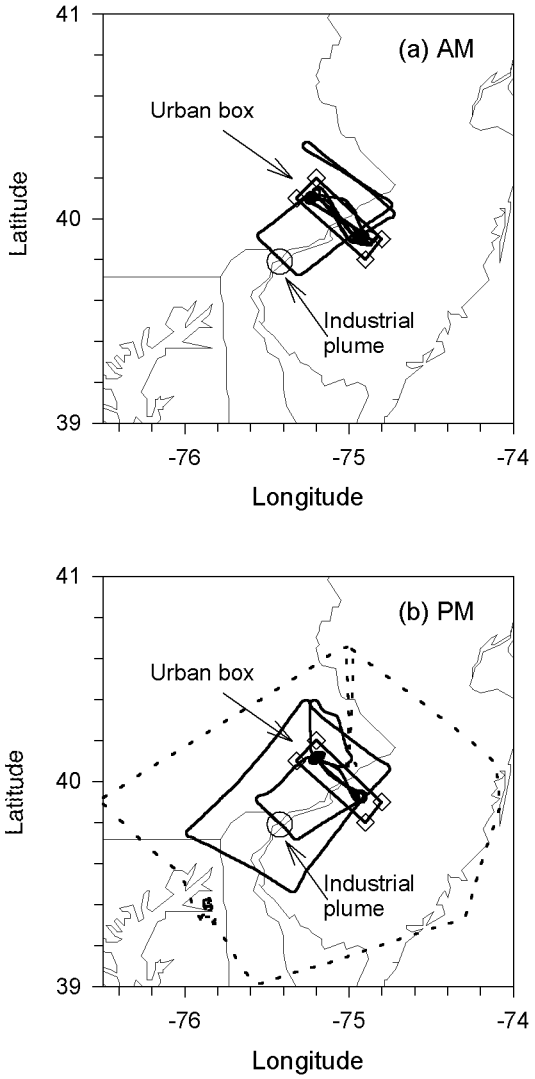

Figure 1. G-1 flight patterns. (a) A typical morning urban flight from July 31. (b) A typical afternoon urban flight from July 31 and a typical regional flight from July 26 (dashed line). The rectangular areas in panels (a) and (b) labeled "Urban Box" enclose a region in which there were vertical profiles and multiple level-flight transects. Outside of this region, most sampling was done between 450 and 900 m altitude. The AM and PM urban flights were typically conducted between 9:00-11:00 and 13:00-15:00 local standard time, respectively. The location of an industrial plume observed on July 31 is marked on panels (a) and (b).

3. RESULTS

Vertical Profiles

Using the G-1 observations, collected northeast of Philadelphia in the rectangular box shown in Fig. 1, we have determined the frequency distribution of pollutants as a function of altitude. Assembling the data in this way leads to a smearing of features, but has the advantage of providing an overview in a compact form. The region that is being examined contains a segment of the Delaware River, industrial facilities near the river, and a heavily traveled interstate highway. Figures 2, 3, 4, and 5 show O_3, NO, SO_2, and the number concentration of accumulation mode aerosol particles as measured with a PCASP probe, respectively. The mixing height was generally below 1000 m in the morning and about 2000 m in the afternoon.

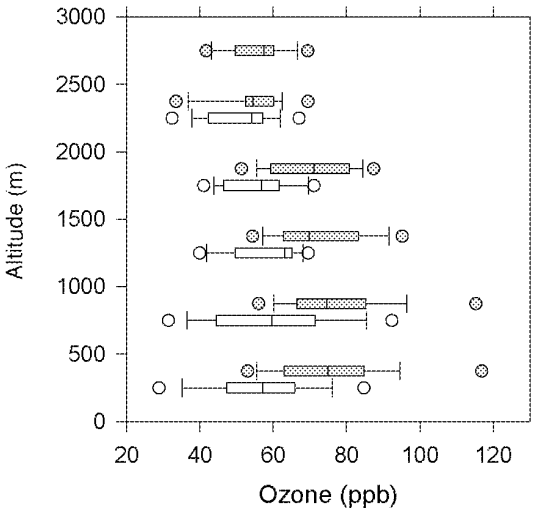

Figure 2. Frequency distribution of O_3 concentration as a function of altitude from 8 urban morning (open bar) and 8 urban afternoon flights (shaded bar). Data is from rectangular area shown in Fig. 1, 20 km NE of downtown Philadelphia. Central portion of bar indicates 25th, median, and 75th percentile values. Caps are 10 and 90th percentile values. Circles are 5 and 95th percentile values.

Median AM O_3 concentration is about 60 ppb with only a hint of an increase in the residual layer above 1000 m. High values below 1000 m are primarily from July 31 which will be examined in more detail below. There is a 20 ppb increase from the morning to afternoon in median O_3 below 1500 m.

Nitric oxide (NO) is a primary pollutant with a strong near-surface source in urban areas. It is in rapid equilibrium with NO_2 and has a several hour lifetime before it is removed from the atmosphere by oxidation reactions of NO_2. The AM profile shows near zero NO concentration above 1000m. At this time of the day this layer is not affected by surface emissions and evidently emissions from the preceding day do not survive overnight (Berkowitz et al., 1998). The very high NO

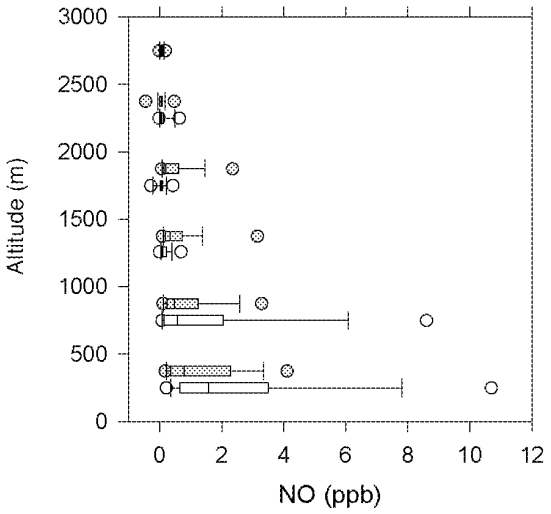

Figure 3. Frequency distribution of NO concentration as a function of altitude. Same format as Fig. 2.

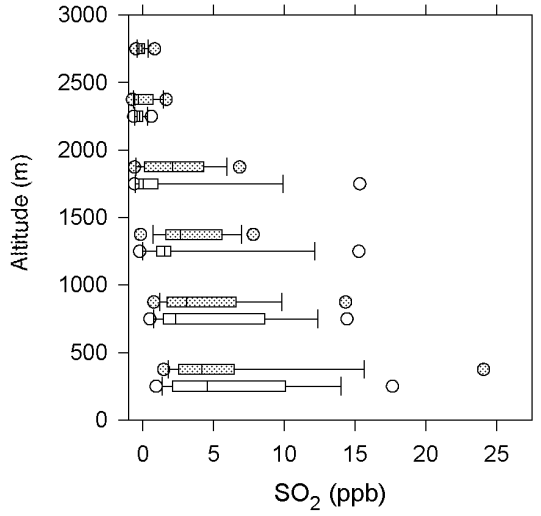

Figure 4. Frequency distribution of SO_2 concentration as a function of altitude. Same format as Fig. 2.

concentrations below 1000 m are due primarily to local highway emissions. In the afternoon NO is mixed up to 2000 m. Below 1000 m, there is a decrease in NO from the morning to afternoon. This feature is seen at surface monitoring sites and is due to a combination of factors: 1) increased emissions in the AM rush hour, 2) a greater boundary layer depth and consequently more room for dilution in the afternoon, and, 3) shift in the NO-NO_2 equilibrium towards NO_2 and more rapid removal of NO_2 in the afternoon.

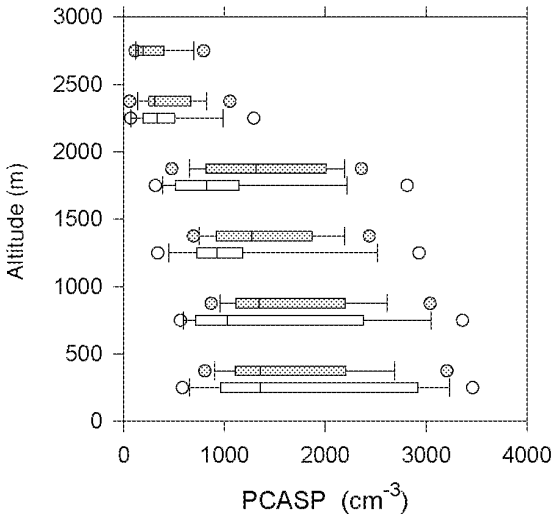

Figure 5. Frequency distribution of accumulation mode aerosol particles as a function of altitude. Same format as Fig. 2.

SO_2, like NO is a primary pollutant, but in contrast to NO, the morning profile shows low, but non-zero, concentration above 1000 m. SO_2 has a longer atmospheric lifetime than NO, and the 2 ppb median concentration between 1000 and 1500 m is from overnight transport. Afternoon levels of SO_2 below 1000 m are comparable to morning levels, unlike NO which decreases.

The concentration of accumulation mode aerosol particles is high. Values above 1000 cm^{-3} give a noticeable reduction in visibility; values above 3000 cm^{-3} are immediately recognized as being very hazy. There were AM flights with PCASP equal to 1000-3000 cm^{-3}, above 1500 m altitude. This material is not local. A trajectory analysis would be helpful in determining the upwind source region. There is an AM to PM increase in PCASP at low altitude which might be linked to same day emissions or photochemistry.

Case Study – July 31

The highest O_3 concentrations observed during G-1 flights occurred on July 31, the final day of an O_3 episode starting on July 27. Weather conditions were hot and dry as typical of an extended drought in the mid-Atlantic region between mid-June and late August. Winds aloft (500-1500 m agl) were from the west and northwest. Day to day variability during this episode is linked to changes in wind speed and the occurrence of up-wind convection. Wind speed decreased on July 31 leading to a jump in O_3 and aerosol concentration (weather and flow description is from Ryan (2000)).

Elevated O_3 occurred along the I95 corridor from Washington to central New Jersey and to a lesser extent through NYC to southern New Hampshire (Ryan, web page).

Figure 6 shows O_3 concentration for an altitude vs longitude cross section of the July 31 AM and PM urban flights. Data is from the rectangular box shown in Fig. 1.

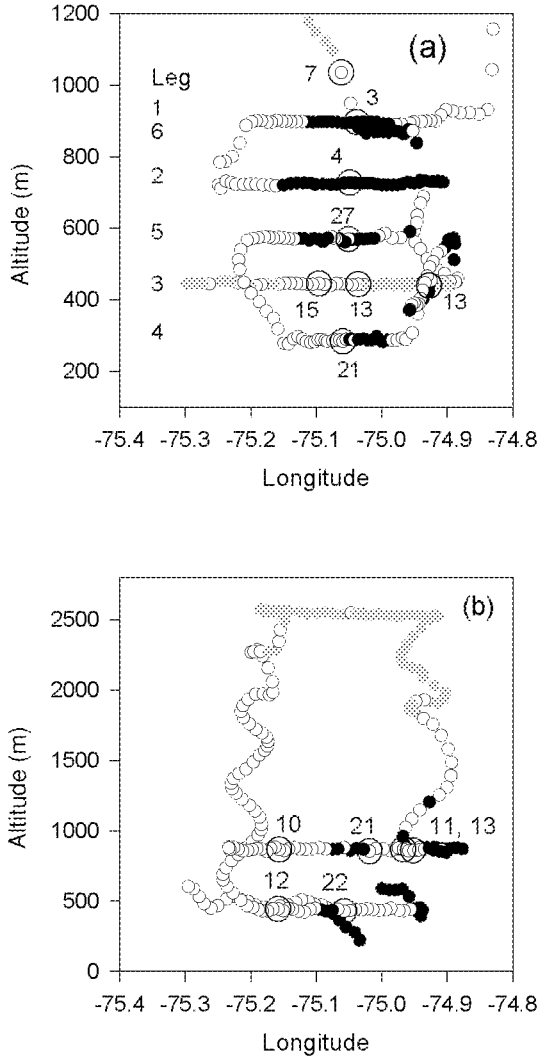

Figure 6. Altitude – Longitude cross section of July 31 in Urban Box (see Fig. 1), each circle is 10 s of flight time (a) AM Flight: Not included are flight segments between 1200 and 2300 m. Ozone color code: Gray circle < 60 ppb; open circle 60-90 ppb; black circle >90 ppb. Transect order given on left. Large circles with numbers nearby are $P(O_3)$ in ppb h^{-1}. (b) PM Flight: Ozone color code Gray circle <70 ppb; open circle 70-120 ppb; black circle >120 ppb.

Circles with numbers next to them indicate the locations of VOC samples and calculated values for $P(O_3)$. Transects are labeled in the order that they occurred. Note that transects 4-6 did not immediately follow 1-3; there was a 1 hour delay.

Ozone on legs 1 and 2 reaches 100 ppb at 9:30 local standard time (LST), with about 75 ppb of that being a "background" value seen on the western portion of this flight. Sonde data collected at 9:00 LST by PNNL at the Baxter surface site (near the G-1 flight pattern) indicates that these legs are above the boundary layer at this time of day. This is consistent with the low NO observed on these legs. A surprising feature is that SO_2 and O_3 are both high and variable as one might expect from a local source region with a high degree of spatial variability. Transect 3 has a region with O_3 concentration below 50 ppb, which is caused by titration from surface NO_x emissions, most likely coming from I95. This feature disappears later in the morning on transects 4 and 5. $P(O_3)$ is very low on transects 1 and 2 because of low NO_x. On transect 3, NO_x concentration is high and O_3 production is actually on the high NO_x side of the ridgeline, ie NO_x inhibited. Higher value of $P(O_3)$, up to 27 ppb/h are calculated later in the morning when photolysis rates are higher and NO_x levels closer to optimum. Figure 6b shows the results of the days photochemistry with a peak O_3 concentration of 133 ppb. Local production is still significant; $P(O_3)$ is between 10 and 22 ppb/h. A comparison of AM and PM O_3 with calculated $P(O_3)$ indicates that local production can more than account for the AM to PM increase. It appears that this region is a net exporter of O_3.

The very highest O_3 concentration observed from the G-1 was not seen in the Philadelphia urban plume, but rather 30 km to the southwest in a plume from an industrial facility located near the Delaware River (see Fig. 1). Figures 7a and b show the concentration of O_3, CO, NO, and SO_2 from encounters with this plume on the morning and afternoon of July 31. In the morning, concentrations of primary pollutants were among the highest seen in the NE-OPS program. A canister sample taken in the AM plume had the highest VOC concentrations observed in the program. On the morning flight, 10 ppb of O_3 was formed on the plume shoulder. In the center of the plume, O_3 was below background due to NO_x titration. Winds on the 31st were extremely light and on the afternoon flight the plume was observed at about the same location as in the morning. Primary pollutants are lower in the afternoon but still elevated relative to regions outside of the plume. O_3 in the afternoon had a peak of 147 ppb, almost 70 ppb above background. This is a rather significant production from what visually appeared from the G-1 to be a single industrial facility.

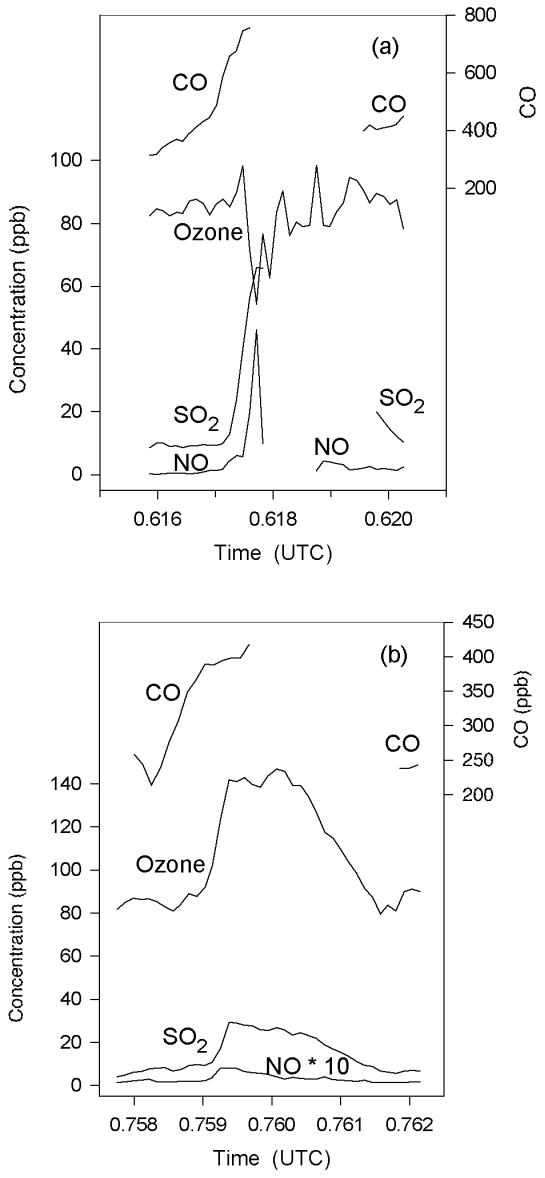

Figure 7. Trace gas concentrations observed on July 31 in an individual plume 30 km southwest of Philadelphia. See Fig. 1 for location. Missing data occurred during instrument zero procedures. (a) Morning flight, (b) Afternoon flight.

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